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**ELECTRICAL TRANSPORT PROPERTIES OF GADOLINIUM
SCANDIUM GALLIUM GARNET**


K. B. SCHWARTZ
A. G. DUBA

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Lawrence
Livermore
National
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Electrical Transport Properties of Gadolinium Scandium Gallium Garnet

K.B. Schwartz and A.G. Duba

Lawrence Livermore National Laboratory

P.O. Box 808

Livermore, CA 94550

ABSTRACT

Electrical conductivity and thermoelectric power are measured on a single crystal of $\text{Gd}_{3.0}\text{Sc}_{1.8}\text{Ga}_{3.2}\text{O}_{12}$ (GSGG) between 1273 and 1673 K. The measurements are made both in air and in controlled atmospheres, and PO_2 varies from $10^{-1.68}$ MPa to $10^{-5.6}$ MPa. The data indicate GSGG may well be a mixed conductor in this temperature and PO_2 range, with n-type electronic conductivity and ionic transport on the oxygen sublattice. Changes in temperature induce long-lived disequilibrium in electrical conductivity of GSGG (over 30 hours at $T < 1373$ K) that can be explained by temperature dependent cation redistribution. The effective activation energy for equilibrium electrical conductivity is $E_a = 2.40 \pm 0.05$ eV, as opposed to values of E_a between 1.8 and 2.2 eV during actual temperature changes. An additional contribution in the equilibrium E_a , due to thermally activated cation redistribution, can account for the higher value seen.

1. INTRODUCTION

Oxides with the garnet structure have found various applications as materials in solid state electronic devices. Studies of their physical properties have concentrated on areas relevant to the technological significance of a particular garnet composition. For ferrimagnetic garnets containing paramagnetic transition metals in one or two of the three cation sites (e.g. $\text{VIII}\{\text{Y}_3\}^{\text{VI}}[\text{Fe}_2]^{\text{IV}}(\text{Fe}_3)\text{O}_{12}$ (YIG); $\{\text{Ca}_3\}[\text{Mn}_2](\text{Ge}_3)\text{O}_{12}$),¹ this has meant emphasis on magnetic and magneto-optical properties. For nonmagnetic aluminate garnets used as solid state laser hosts like $\{\text{Y}_3\}[\text{Al}_2](\text{Al}_3)\text{O}_{12}$ (YAG), the spectroscopic properties of laser active rare-earth metals contained in the host garnet have attracted the most attention. And, for gallate compositions which can be used as substrate materials upon which layers of ferrimagnetic garnet can be grown, research has been directed towards mechanical properties and the relationship between chemical variations and lattice parameters of compositions based on $\{\text{Gd}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$ (GGG).

The transport properties and kinetics of synthetic garnets have been examined insofar as they give information about the defect structure and its effect on the physical properties of interest. The kinetics of magnetic garnets have been studied intensively because of the effects of point defects (e.g. chemical impurities, lattice variations, and changes in valence state of transition metal cations) on the electronic properties of the materials. Monitoring changes in optical, magnetic, and electrical properties as a function of temperature, external atmosphere, or impurity content has yielded some understanding of the relationship between defect structure and transport properties in ferrite garnets.²⁻⁸ For nonmagnetic garnets the scope of the studies has been more limited. The passivation of color centers and other

optical impurities in YAG by high-temperature processing in controlled atmospheres has given information on important defects and transport properties in this composition.⁹⁻¹³ But for aluminate and gallate garnets there have been very few data reported on electrical conductivity.¹⁴⁻¹⁶

The present communication describes a study of the ac electrical conductivity (σ) and thermoelectric power or Seebeck coefficient (α) of a single crystal of $\text{Gd}_3\text{Sc}_{1.8}\text{Ga}_{3.2}\text{O}_{12}$ (GSGG) as a function of PO_2 between 1273 and 1673 K. GSGG is a material that has attracted recent interest as a potential host for co-doping Cr^{3+} in Nd^{3+} lasers,¹⁷⁻¹⁸ and the substitution of Sc for Ga in GGG has also been investigated for the alteration of lattice parameters to increase its suitability as a substrate material.¹⁹ The present study, along with comparison to electrical conductivity and atomic transport data of previously studied garnets, thus gives some information on possible conduction mechanisms and the predominant point defects in GSGG.

2. EXPERIMENTAL

A single crystal sample of GSGG was cut from a boule grown by the Czochralski method by the Crystal Products Division of Union Carbide Corporation (sample #SD175-17-17). Major element determination performed using inductively coupled plasma spectrochemical analysis yielded a chemical formula of $\text{Gd}_3\text{Sc}_{1.8}\text{Ga}_{3.2}\text{O}_{12}$ with errors of $\pm 1\%$ for Ga_2O_3 and Gd_2O_3 and $\pm 6\%$ for Sc_2O_3 . Trace element analysis, performed by dc arc emission spectroscopy, is given in Table I. The sample shape was a rectangular plate of dimensions 3.54 x 4.20 x 0.27 mm. The sample was cut with a diamond saw, ground with SiC paper down to 600 grit, polished with 1 μ m diamond slurry in kerosene, and then cleaned in

succession in boiling HCl, acetone, and ethanol.

The previously described electrical conductivity apparatus²⁰ contains a spring loaded sample holder inside a gas-tight alumina tube. The GSGG crystal was sandwiched between 0.001" (25.4 μm) thick Pt foils before being placed in the sample holder to insure good electrical contact with the Pt electrodes. These electrodes are attached to Pt wires, used as electrical leads, and to Pt-10%Rh wires, to complete a thermocouple junction. The temperature is thus measured at each side of the sample. Resistance and thermal emf are measured by the two-probe bridge technique with a Hewlett-Packard LCR meter (model 4274) and a computerized data acquisition system.²¹ The ac resistance measurements are made at 10^2 , 10^3 , and 10^4 Hz with an applied voltage of 5 V RMS. The HP 4274 LCR meter is accurate to $\pm 2\%$, and it is estimated that the resultant electrical conductivity data has a maximum error of ± 0.01 of a log unit in S/m over the entire range of temperature and oxygen pressure. The actual sample resistance varies from 337 to 66,400 ohms.

The electrical conductivity and thermoelectric power data were collected in four different atmospheres: air, 1.0% O_2 /99.0% Ar, 0.1% O_2 /99.9% Ar, and dry, 99% pure CO_2 . The O_2 /Ar runs used pre-mixed tanks whose gas ratios were measured using an oxygen analyzer. For experiments using O_2 /Ar mixtures or CO_2 , the gas was flowed through a drier/purifier (Matheson type 451), then introduced into the sample chamber at one end and flowed by the sample to an outlet on the other side. For the experiment in air the intake and outlet hoses were removed and the apparatus was left open to the laboratory environment. The P_{O_2} of pure CO_2 is a function of temperature, and varies from $10^{-4.2}$ MPa at 1623 K to $10^{-5.6}$ MPa at 1333 K. For the other experiments the oxygen pressure is constant over the entire temperature range.

For thermoelectric power measurements the sample assembly was moved in

either direction relative to the peak temperature region of the furnace to create a temperature gradient across the sample. The thermoelectric power or Seebeck coefficient (α) was calculated from a linear least-squares fit of ΔV vs ΔT consisting of at least 25 data points with a maximum $\Delta T < 20$ K. In accordance with convention,

$$\alpha = -\Delta V / \Delta T = (V_h - V_c) / (T_c - T_h), \quad (1)$$

so that the sign of α corresponds to the sign of the majority charge carrier.²²

3. RESULTS

It was continually noted during this set of experiments that significant, long-lived disequilibrium was introduced into the system during temperature cycles at constant PO_2 for heating or cooling rates as low as 0.5–2.5 K/min. Electrical conductivity was always significantly lower for the initial heating than for the subsequent cooling for continuous changes in temperature at all values of PO_2 . This indicates that even slow changes in temperature introduce readily measurable disequilibrium into the system and that the defect structure changes with temperature even at constant PO_2 . Because of this effect, care was always taken that σ had equilibrated after a change in temperature before readings were taken of the equilibrium electrical conductivity (σ_{eq}). It was also observed that to obtain reproducible σ_{eq} measurements the sample first needed to be equilibrated in the range 1573–1673 K in each experimental atmosphere. Similar behavior was noted in a study of the electrical conductivity of YIG.⁵ After this high temperature anneal σ_{eq} was very reproducible throughout the 1273–1673 K temperature range.

The results of σ_{eq} measurements at 10 kHz are shown in Fig. 1. The

least-squares fit of the data in each atmosphere to the Arrhenius relation

$$\log \sigma_{eq} = \log \sigma_0 - E_a/2.3kT \quad (2)$$

demonstrates that electrical conductivity in GSGG is a thermally activated process. In all four atmospheres $E_a = 2.40 \pm 0.05$ eV, with no significant deviation in E_a as a function of PO_2 . However, σ_{eq} is clearly affected by PO_2 , with conductivity increasing as PO_2 is lowered. Plots of $\log \sigma_{eq}$ vs $\log PO_2$ at four different temperatures are shown in Fig. 2. Over this very restricted range in PO_2 space a linear relationship is seen, with a very shallow slope of approximately $-1/16$ at 1332 K decreasing to approximately $-3/32$ at 1622 K. Unfortunately, attempts to collect data at lower PO_2 were not successful, as s would not equilibrate in CO-CO₂ gas mixtures, but just continued increasing with time. This indicates the instability of GSGG at low PO_2 , which is consistent with findings that YIG is unstable at $PO_2 < 10^{-5}$ MPa at 1543 K.²³

An increase in σ_{eq} with decreasing PO_2 is often associated with the creation of oxygen vacancies ($V_O^{\bullet\bullet}$),²⁴ enhancing n-type electronic conductivity. That the sign of the Seebeck coefficient α in all atmospheres is negative is consistent with the hypothesis that this is occurring in the present experiments. Plots of α vs $1/T$ (Fig. 3) show that the thermopower is not independent of temperature, as would be expected for the electron-hopping (small polaron) conduction mechanism containing a fixed number of charge carriers,²⁵ and as exhibited in $\{Ca_3\}[Mn_2](Ge_3)O_{12}$.²⁶ These data, to be discussed below, suggest that a multi-faceted defect structure is controlling electrical conduction in GSGG.

Since the sample could not rapidly return to equilibrium, as indicated by electrical conductivity measurements after changes in temperature, all changes in temperature were followed by a wait for sample equilibration. Some attention was also paid to the behavior of s under non-equilibrium conditions.

When the temperature was changed at ~ 2.5 K/min, the measured value of E_a was always in the range 1.8 to 2.2 eV with an error of ± 0.05 eV (Fig. 4). Though the measured value of E_a did vary, it was always significantly below the value of E_a obtained from σ_{eq} . Electrical conductivity always continued to increase at the end of a temperature rise and decrease at the end of a temperature fall. In the measurements shown in Fig. 4, where $\Delta T = -155$ K, σ continued to decrease for over 40 hours after the temperature stabilized, finally equilibrating at $\log[\sigma \text{ (S/m)}] = -2.87$ at 1363 K, an increase in resistance of over 40% of the resistance at 1363 K during the temperature ramp. Equilibration times were related to temperature, with σ stabilizing in < 5 hours above 1573 K and taking > 30 hours to equilibrate at $T < 1373$ K. The value of the external PO_2 had no significant effect on equilibration times following temperature changes. In contrast, σ equilibrated after changes in external PO_2 within a matter of minutes.

A frequency dispersion for σ_{eq} was observed for data collected at the higher temperatures and for data collected in air. For GSGG in CO_2 or the O_2/Ar mixtures σ_{eq} was 8 to 15% lower at 100 Hz than at 10 kHz for temperatures above 1523 K. At lower temperatures no frequency dispersion was seen in these atmospheres, and no frequency dispersion was detected between 10 kHz and 100 kHz. In air, σ_{eq} was 10-20% higher at 100 Hz than at 10 kHz, with no dispersion between 1 kHz and 100 kHz. This unexpected result in air may be due to the presence of water vapor in contact with the sample, and the results in air should be compared to the other data with caution due to the known effects of hydrogen on the defect structure of garnets.^{3,9-13}

4. DISCUSSION

The increase in σ_{eq} with decreasing PO_2 suggests that $V_O^{\cdot\cdot}$ may have a role in the conduction mechanism for GSGG. It has been shown that $V_O^{\cdot\cdot}$ are the most important native defect in YIG,^{4,23} and that generation of $V_O^{\cdot\cdot}$ as a donor species increases the concentration of electrons in both n-type and p-type YIG, whose electrical conductivity behavior is best explained by a large polaron model.^{5,27} A large polaron model would not be expected for GSGG due to the absence of transition metals as a major constituent. Indeed, electrical conductivity measurements on garnets that contain transition metals on only one crystallographic site, $\{Ca_3\}[Mn_2](Ge_3)O_{12}$, are consistent with hopping of small polarons on the Mn sublattice.²⁶ But n-type conductors controlled by the neutrality equation

$$\underline{n} = 2[V_O^{\cdot\cdot}], \quad (3)$$

where \underline{n} is the concentration of n-type carriers, have a $\log \sigma$ vs $\log PO_2$ dependence with a slope of $-1/6$.^{28,29} The $\log \sigma$ vs $\log PO_2$ data for GSGG, though limited in PO_2 space, give a much shallower slope of about $-1/16$. This does not rule out electronic conduction in GSGG, but it does suggest that additional mechanisms must also be at work.

If electronic conduction is occurring exclusively in GSGG, the thermoelectric measurements indicate that \underline{n} is not constant. As mentioned above, electron hopping in a system with constant \underline{n} leads to a temperature-independent value of α .^{25,26} The observed decrease in $|\alpha|$ implies that \underline{n} is increasing with increasing temperature, since for electron hopping

$$\alpha = -k/e \ln[(1-\underline{c})/\underline{c}], \quad (4)$$

with

$$\underline{c} = \underline{n}/N, \quad (5)$$

N being the concentration of available sites for the hopping electron and e the elementary charge. This view of new n -type carriers being generated with increasing temperature implies an increase in $[V_O^{\bullet\bullet}]$ if the mechanism suggested above, $n=2[V_O^{\bullet\bullet}]$, is valid. Work on YIG has shown that at elevated temperatures ($T > 1173$ K), $[V_O^{\bullet\bullet}]$ does increase with increasing temperature at constant PO_2 .^{23,30}

In suggesting possible conduction mechanisms for GSGG, one cannot rule out the presence of a component of ionic conductivity on the basis of the present data. No previous work on YAG or GGG has yielded a definitive conduction mechanism, but in both cases ionic conductivity has been suggested.^{14,15} There is some evidence in the present experiments for ionic transport in GSGG. The frequency dispersion for σ_{eq} between 100 Hz and 10 kHz, which disappears at higher frequency, is consistent with ionic conductivity.^{31,32} The temperature dependence of α is reported in $\{Ca_{3-x}Y_x\}[Mn_2](Ge_3)O_{12}$ at high temperatures, and in that case the behavior is attributed to increasingly mobile ionic defects.²⁶ And, the very shallow slope of $\log \sigma_{eq}$ vs $\log PO_2$ plots may be explained if GSGG is a mixed conductor, with PO_2 independent conduction in an electrolytic zone at higher PO_2 grading to pure n -type electronic conduction at lower PO_2 . The region in PO_2 space shown in Fig. 2 would then be a transition region, with the expectation of a steeper slope at lower PO_2 . Naturally, a measurement of the ionic transference number²⁹ would be essential in confirming the validity of this hypothesis. There are no reliable cation diffusion data on synthetic rare earth garnets, but reported diffusion rates for oxygen and fluorine anions in YIG are on the order of 10^{-13} m²/sec at 1673 K.^{33,34} These values are high enough to generate values of ionic conductivity similar to those seen in GSGG.

A mechanism is also needed to explain the long relaxation times after

temperature changes and the two measured values of E_a , one associated with the temperature dependence of σ during actual temperature ramps ($E_a = 2.0 \pm 0.2$ eV) and the other associated with the temperature dependence of σ_{eq} ($E_a = 2.40 \pm 0.05$ eV). Though changes in temperature can be associated with changes in $[V_O^{\bullet}]$, the rapid equilibration of s with changes in PO_2 indicate V_O^{\bullet} equilibration cannot explain such long-lived disequilibrium. One possibility is temperature dependent cation redistribution, either short-range ordering of $[Sc^{3+}]$ and $[Ga^{3+}]$ cations on the octahedral sublattice or disordering of Sc^{3+} over two or all three of the cation sites. Changes in site occupancy of the cations in GSGG could have an impact on electrical conductivity, and relaxation times would be reflecting thermally activated cation diffusion to achieve the equilibrium distribution at a given temperature. An order-disorder mechanism would add an additional contribution to the equilibrium E_a , accounting for the two values seen in GSGG. Cation ordering between $[Fe^{3+}]$ and $[Al^{3+}]$ has been reported previously to be present on a large scale in a silicate garnet, giving rise to optical birefringence and a reduction in symmetry from a cubic to an orthorhombic space group.³⁵ Furthermore, cation redistribution of Fe^{3+} , Al^{3+} , and Ga^{3+} over the octahedral and tetrahedral sites is known to affect other physical properties, such as magnetization in ferrite garnets.⁷ In addition, Sc^{3+} has been reported in all three crystallographic sites in various ferrite and gallate garnets.^{19,36} The large reduction in relaxation times for an endmember composition, $\{Y_3\}[Ga_2](Ga_3)O_{12}$ (YGG)³⁷, seems to support a cation redistribution model for the occurrence of long relaxation times in GSGG.

The activation energies seen in GSGG are consistent with either an ionic or electronic conduction mechanism. For anion and V_O^{\bullet} diffusion, E_a has been found in the 2.8-3.4 eV range in YIG.^{4,33,34} The intrinsic band gap for GSGG would be expected to be approximately 6.5 eV, the value for YAG determined by optical

absorption measurements.³⁸ But a conduction mechanism dependent on defects would greatly lower this value. For small polaron conduction in Gd_2O_3 , a mechanism similar to electron hopping on the $\{\text{Gd}^{3+}\}$ sublattice in GSGG, E_g was found to be 1.57 eV.³⁹ This mechanism is plausible due to edge sharing of $\{\text{Gd}^{3+}\}$ sites in the garnet structure and reports of the reduction of eight-coordinated rare-earth cations associated with the creation of O^- -centers in rare-earth doped YAG.⁹ A variation on this theme would have the electron freed by the creation of the O^- center (O_O^- in Kröger-Vink notation) trapped at an $\text{V}_\text{O}^\bullet$, a mechanism also suggested to occur in YAG.¹¹ An alternative model could be based on transition metal impurities with energy levels located approximately in the middle of the band gap. Such a mechanism has been suggested for MgO , where the removal of an electron from the Fe_{Mg}^x state into the conduction band is associated with an $E_g = 3.8$ eV for n-type electronic conductivity.⁴⁰

5. CONCLUSION

Electrical conductivity measurements in GSGG indicate that a complicated system is present, in which several chemical and structural considerations may be impacting the results. No single defect seems to be dominating conductivity even over this limited PO_2 range. It is likely that $\text{V}_\text{O}^{\bullet\bullet}$, which plays such an important role in the transport properties of other garnets, is a significant defect in GSGG. Additional work must address the relative importance of other mechanisms, since GSGG may well be a mixed conductor in this temperature and PO_2 regime, and O^{2-} transport and disorder on the cation sublattice cannot be eliminated as important factors in explaining the present results.

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FIGURE CAPTIONS

1. Equilibrium electrical conductivity of GSGG in four different atmospheres at 10 kHz between 1273 and 1673 K. Data points are 4 times larger than the estimated error. Effective activation energies associated with each data set are 2.37 ± 0.01 eV in air, 2.37 ± 0.02 eV in 1.0% O_2 /Ar, 2.45 ± 0.02 eV in 0.1% O_2 /Ar, and 2.36 ± 0.02 eV in CO_2 .
2. $\log \sigma_{eq}$ vs. $\log PO_2$ for GSGG at four different temperatures. Slopes given are derived from a linear least-squares fit in each atmosphere.
3. Thermoelectric power or Seebeck coefficient (α) of GSGG in three different atmospheres between 1350 and 1673 K.
4. Electrical conductivity of GSGG in 1.0% O_2 /Ar during a lowering of temperature from 1513 to 1358 K at ~ 2.5 K/min. The effective $E_a = 2.06 \pm 0.01$ eV, significantly lower than seen for σ_{eq} vs. $1/T$. Conductivity continued to decrease for over 40 hours after the temperature stabilized, equilibrating at $\log \sigma = -2.87$ (see text).

TABLE I

SPECTROCHEMICAL ANALYSIS OF GSGG

Element	ppm (atomic)
Y	5
B	4
Fe	0.2
Mg	0.08
Mo	0.05
Si	0.02
Ca	0.01
Mn	0.009
Cu	0.008
Sr	0.006

The above elements were detected to $\pm 100\%$.

Element	ppm (atomic)
Na	<2
Ce,Nd,Tb,Lu,Ta	<0.3
Zr	<0.3
Pr,Nb	<0.2
Sm,Ho	<0.1
Zn,As	<0.07
Be	<0.05
Cd	<0.04
La,Dy,Tm	<0.03
Al,Sb	<0.02
Ti,V,Cr,Co,Ni,Ge,In	<0.01
Sn,Ba,Eu,Er,Yb,Pb,Bi	<0.01

The above elements were not detected. The concentration given is that needed to confirm the element.

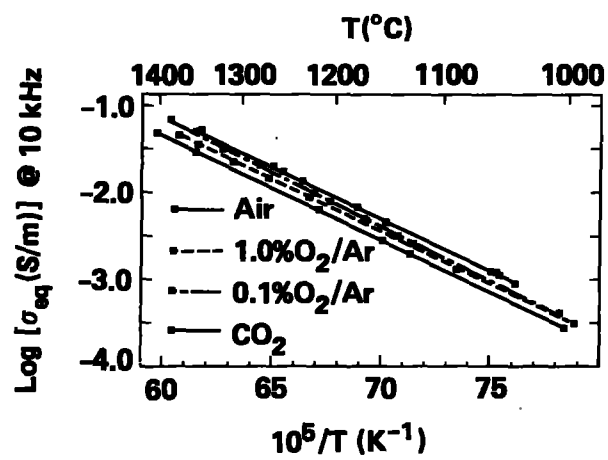


Figure 1

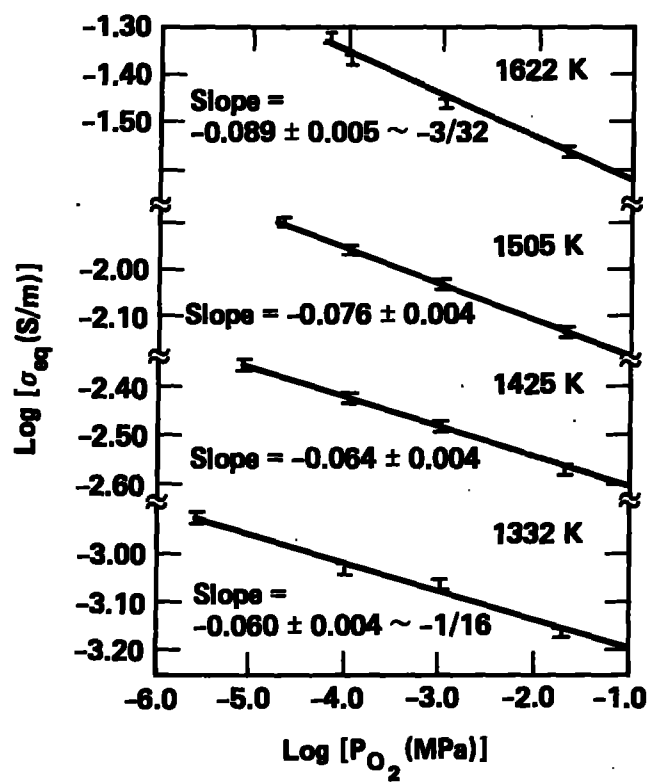


Figure 2

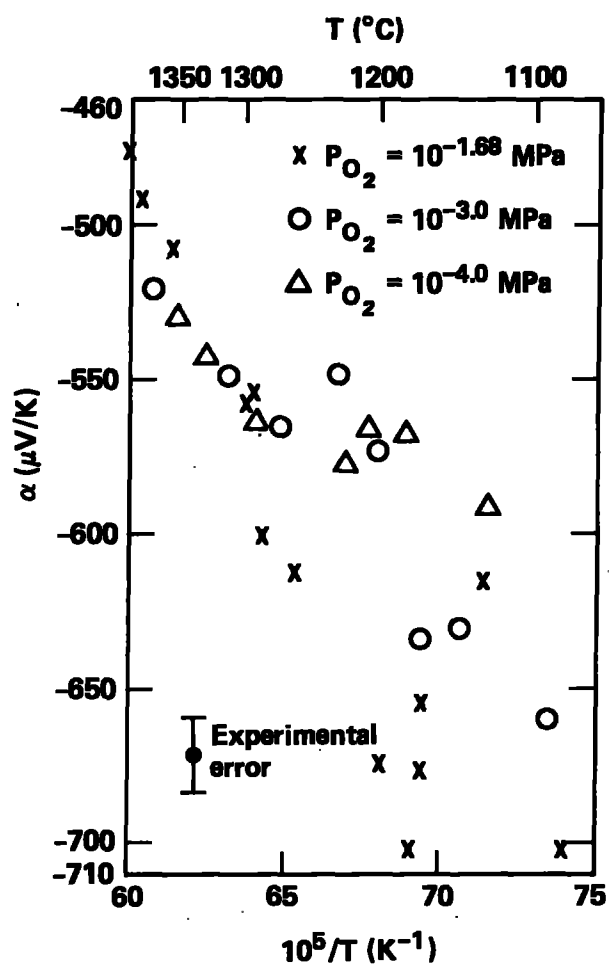


Figure 3

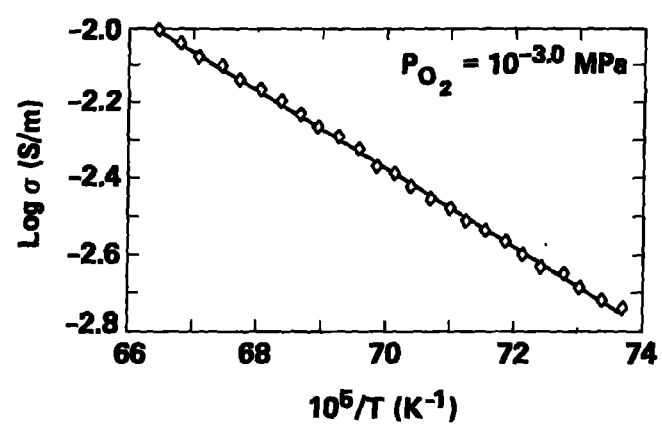


Figure 4